

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 962 320 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication: 08.12.1999 Bulletin 1999/49
(51) Int. Cl.⁶: B41J 2/16

(21) Application number: 99110640.2

(22) Date of filing: 02.06.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 03.06.1998 JP 15438998
03.06.1998 JP 15439098
03.06.1998 JP 15439198

(71) Applicant:
CANON KABUSHIKI KAISHA
Ohta-ku, Tokyo (JP)

(72) Inventors:
• Makoto, Terui,
c/o Canon Kabushiki Kaisha
Tokyo (JP)
• Hirokazu, Komuro,
c/o Canon Kabushiki Kaisha
Tokyo (JP)
• Norio, Ohkuma,
c/o Canon Kabushiki Kaisha
Tokyo (JP)

(74) Representative:
Pellmann, Hans-Bernd, Dipl.-Ing. et al
Patentanwaltsbüro
Tiedtke-Bühling-Kinne & Partner
Bavariaring 4
80336 München (DE)

(54) Ink-Jet head, ink-jet head substrate, and a method for making the head

(57) In an ink-jet head substrate including a thermal effect section for applying thermal energy to liquid to form a bubble in the liquid, the thermal effect section being connected with a nozzle for discharging the liquid, an electrothermal transducer for generating the thermal energy, and a pair of electrodes, a resin layer composed of a polyether amide is formed on the surface of the substrate.

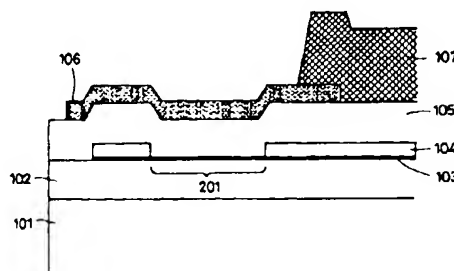


FIG. 2

EP 0 962 320 A1

Description

BACKGROUND OF THE INVENTION5 Field of the Invention

[0001] The present invention relates to an ink-jet head for discharging liquid through an orifice and for forming droplets, an ink-jet head substrate, and a method for making the head.

10 Description of the Related Art

[0002] Japanese Patent Application Laid Open No. 54-51837 discloses an ink-jet recording process, which is different from other ink-jet recording processes. That is, thermal energy is applied to liquid. The heated liquid forms a bubble, and a force generated by the formation of the bubble discharges a droplet of the liquid through an orifice at the tip of an ink-jet head. The droplet adheres on a recording medium to record information.

[0003] The ink-jet head used in this recording process has a liquid-discharging section having an orifice for discharging droplets and a liquid channel provided with a heating section for imparting thermal energy to the liquid, an exothermic element as an electrothermal transducer which generates pressure capable of discharging ink, electrodes for applying electrical energy, and a substrate for holding these components. The head has a heat-accumulating layer provided between the exothermic element and the substrate, and an upper protective layer for protecting the exothermic element and the electrodes from ink.

[0004] Japanese Patent Application Laid-Open No. 59-194866 discloses an organic topmost layer formed on an upper protective layer, that is, a surface layer of the substrate. The organic layer has small amounts of pinhole defects and has high coverage, although the layer does not have thermal resistance. Organic materials proposed as the surface layer of the substrate are silicone resins, fluorinated resins, polyamide resins, polyimide resins, epoxy resins, phenol resins, Zirox resins, triazine resins, and BT (bismaleimide-triazine) resins. Among these, polyimide resins are generally used since the resins can readily form films and have high ink resistance.

[0005] In recent ink-jet processes, use of various types of paper, for example, plain paper, is required. Thus, inks used in these processes have inherent properties which are different from that of conventional inks. Such inks readily spread on plain paper to decrease the print density compared with coated paper. The dye content in the ink must be increased to enhance the print density. The ink having a high dye content prompts precipitation or adhesion of the dye at a nozzle tip. Thus, urea as a humectant is added to the ink having a high dye content so that the dye does not adhere.

[0006] A head containing a urea-containing ink which is designed based on the above-described concept will break down after a long continuous operation. In the head, at failure, the polyimide resin layer on the substrate surface is lost. Thus, the polyimide resin is unsuitable for urea-containing inks. Accordingly, required organic resins must facilitate formation of films, and must have high resistance against urea-containing inks and thermal resistance.

[0007] In addition, inks capable of recording on various media, other than plain paper, are desirable. Furthermore, alkaline inks will be developed in future, instead of conventional neutral inks. Thus, ink-jet recording systems must allow use of a wide variety of inks.

[0008] Japanese Patent Application Laid-Open No. 61-154947 discloses a method for making an ink-jet head, in which a solid layer having a channel pattern is formed on a substrate, a material for forming a channel is provided thereon, and then the solid layer is removed. When a positive resist is used as the patterned solid layer and when an epoxy resin is used as the ink channel component, an aqueous inorganic or organic alkaline solution or a polar solvent is used to remove the positive resist. Use of a metallic material, such as aluminum, in the substrate and the top board has heat accumulation and material cost advantages compared to Si substrates. Such a metallic material may be dissolved in the aqueous inorganic or organic alkaline solution. Thus, use of a polar solvent such as ethyl cellosolve (ethylene glycol monoethyl ether) is preferable.

[0009] Since organic polar solvents dissolve polymeric compounds not soluble in nonpolar solvents, the use of organic polar solvents in production of ink-jet heads will form cracks and voids in the organic layer on the substrate surface or will completely dissolve the organic layer. Accordingly, the material used as the surface layer of the substrate must have resistance against a solution for removing the positive resist, in addition to resistance against the alkaline ink.

SUMMARY OF THE INVENTION

[0010] Accordingly, it is an object of the present invention to provide an ink-jet head substrate having a stable surface layer which is highly resistive against alkaline inks and polar solvents.

[0011] It is another object of the present invention to provide an ink-jet head.

[0012] It is still another object of the present invention to provide a method for making an ink-jet head.

[0013] An aspect of the present invention is an ink-jet head substrate including a thermal effect section for applying thermal energy to liquid to form a bubble in the liquid, the thermal effect section being connected with a nozzle for discharging the liquid, an electrothermal transducer for generating the thermal energy, and a pair of electrodes, wherein a resin layer composed of a polyether amide is formed on the surface of the substrate.

5 [0014] Another aspect of the present invention is an ink-jet head including a nozzle for discharging liquid, a liquid channel connected with the nozzle, a substrate having a pressure-generating element for discharging the liquid, the liquid channel including the pressure-generating element, and a liquid channel component bonded to the substrate to form the liquid channel, wherein the substrate has a resin layer comprising a polyether amide resin at the bonded section to the liquid channel component.

10 [0015] A third aspect of the present invention is a method for making an ink-jet head including a nozzle for discharging liquid, a liquid channel connected with the nozzle, a substrate having a pressure-generating element for discharging the liquid, the liquid channel including the pressure-generating element, and a liquid channel component bonded to the substrate to form the liquid channel, the method including the steps of forming a polyether amide layer on the pressure-generating element of the substrate, forming a liquid channel pattern on the polyether amide layer using a soluble resin,

15 forming a covering resin layer for forming a liquid channel wall on the liquid channel pattern, forming the nozzle in the covering resin layer above the pressure-generating element, and dissolving the liquid channel pattern.

[0016] In the ink-jet head, the liquid channel component may be a top board having a groove for forming a part of the liquid channel.

[0017] The top board may be pressed and fixed to the substrate by an elastic member.

20 [0018] The ink-jet head in accordance with the present invention may be of an edge shooter type and of a side shooter type.

BRIEF DESCRIPTION OF THE DRAWINGS

25 [0019]

Fig. 1 is a plan view of an ink-jet head substrate in accordance with the present invention;

Fig. 2 is a cross-sectional view taken along line II-II in Fig. 1;

Fig. 3 is a cross-sectional view of an ink-jet head along the liquid channel;

30 Fig. 4 is a schematic view of an ink-jet head of Example 3;

Fig. 5 is an isometric view of an ink-jet head substrate of Example 4;

Figs. 6 to 11 are cross-sectional views for illustrating a method for making an ink-jet head of Example 4;

Fig. 12 is a schematic isometric view of an ink-jet head of Example 5;

Fig. 13 is a schematic isometric view of an orifice plate of Example 6;

35 Fig. 14 is a schematic isometric view of an ink-jet head of Example 6; and

Fig. 15 is a schematic isometric view of an orifice plate of Example 7.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

40 [0020] Fig. 1 is a plan view of an ink-jet head substrate in accordance with the present invention, and Fig. 2 is a cross-sectional view taken along line II-II in Fig. 1. Fig. 3 is a cross-sectional view of an ink-jet head using the substrate shown in Fig. 1.

[0021] With reference to Figs. 2 and 3, a substrate 101 is generally composed of silicon, ceramic or metal. An electrothermal transducer consisting of an exothermic layer 103 and electrode layers 104 is provided above the substrate 101. The exothermic layer 103 is composed of, for example, TaN or HfB₂, and the electrode layers 104 are composed of, for example, aluminum. When a voltage is applied to the electrothermal transducer based on driving information, the portion of the exothermic element 201 not covered with the electrode layers 104 is heated. A heat-accumulating layer 102 composed of SiO₂ or the like is provided on the substrate 101 so as to effectively conduct the heat generated in the exothermic element 201 to ink. Thus, the exothermic element 201 is formed on the heat-accumulating layer 102. In this embodiment, three protective layers 105, 106 and 107 are formed on the electrothermal transducer to protect the exothermic element 201 from electrolytic corrosion, although the number of the protective layers is not limited. The first protective layer 105 is composed of inorganic insulator such as SiO₂ and the second protective layer 106 is composed of Ta or the like and functions as a cavitation resistant layer. Furthermore, the third protective layer 107 composed of a polyether amide is provided in order to improve ink resistance of the first protective layer 105. It is preferable that the polyether amide protective layer 107 be not provided right above the exothermic element 201 in view of thermal resistance. Thus, the polyether amide film is patterned as shown in Fig. 1. The patterning is preferably performed by any dry etching process. In particular, an oxygen plasma ashing process is suitable for highly precise patterning. The polyether amide protective layer 107 is generally formed by coating of a polyether amide solution, and the residual solvent content

affects the ink resistance of the protective layer 107. According to results by the present inventors' research, a residual solvent content of 4% or less causes high resistance against the above-mentioned alkaline inks. In addition, a residual solvent content of 0.5% or less causes high resistance against the above-mentioned polar solvents. Such preferable residual solvent contents can be achieved by baking of the polyether amide film at a high temperature. When the polyether amide film is baked at a temperature which is higher than the glass transition temperature (230°C) or more of the polyether amide, the layer has high resistance against both the alkaline inks and the polar solvents.

[0022] With reference to Fig. 3, a top board 108 having grooves is assembled on the protective layers so as to form ink channels 109 of the ink-jet substrate. The grooved top board 108 is formed by etching of glass or molding of a resin, such as polysulfone or polyether sulfone. When the grooved top board 108 is formed by resin molding, the grooved top board 108 may be pressed onto the substrate using an elastic member not shown in the drawing, such as a presser bar spring to correct a warp formed during the molding. Since the polyether amide protective film 107 extends to the bonding sections to the grooved top board 108, the grooved top board 108 can be more firmly bonded to the substrate. In a conventional configuration, a second protective layer composed of thallium is provided at bonding sections of a grooved top board, and the thallium has a Young's modulus of 1.90×10^4 kgf/cm². In contrast, the polyether amide used in the present invention has a Young's modulus of 260 kgf/cm² and is substantially the same as that of polysulfone which is generally used in the grooved top board 108. The polyether amide protective layer 107 is also deformed together with the grooved top board 108 by the pressing force to improve the bonding state. Since this Young's modulus is lower than that (300 kgf/cm²) of a polyimide used in a conventional third protective layer, the bonding state in the present invention is improved compared to a configuration using a polyimide as the third protective layer.

[0023] A single protective layer configuration may also be employed in the present invention. This embodiment shows an edge shooter-type configuration in which discharge nozzles (not shown in the drawing) are formed at the ends of the ink channels 109. The present invention is also applicable to a side-shooter type head having discharge nozzles provided above an exothermic element.

[0024] Experiments for investigating the ink resistance of the polyether amide film will now be described.

Experiment 1

[0025] A SiO₂ film having a thickness of 2.5 μm was formed on a Si wafer substrate by thermal oxidation. A 2.5-μm thick polyether amide film of HIMAL HL-1200 (Trade Name by Hitachi Chemical Co., Ltd.) was formed at the shaded section in Fig. 3 by the following steps. The substrate was cleaned and dried, and then a polyether amide solution (solvent: n-methyl-2-pyrrolidone) having a viscosity of 500 cP was coated onto the thermally oxidized SiO₂ film using a spinner. The solvent was preliminarily removed at 70°C for 30 minutes. The preliminarily dried substrate was baked under the conditions shown in Table 1 to prepare a plurality of samples. The residual solvent content in these films was determined by gas chromatography. Using a testing ink, which was composed of 5 percent by weight of ethylene glycol, 5 percent by weight of urea, and the balance being water, a preservation test at 60°C and a pressure cooker test (PCT) were performed to observe the state of each film and a change in thickness of the film. The results are shown in Table 1.

[0026] As shown in Table 1, all the polyether films did not disappear after the preservation at 60°C for three months and after the PCT. For comparison, a 2.5-μm thick polyimide film of Photoneece (trade name, by Toray Industries, Inc.) was baked at 400°C and subjected to the preservation test at 60°C for three months and the TCT test. The Photoneece film disappeared after the preservation test. When the residual solvent content in the polyether amide film was 4.0% or less, no disappearance of the film was observed although the film was swelled by water in the tested ink.

[0027] These results show the polyether amide film in accordance with the present invention has high alkaline resistance, and particularly high resistance when the residual solvent content in the polyether amide film is 4.0% or less.

Table 1

Baking Conditions	Residual Solvent Content in Film (%)	Change (μm) in Thickness from Initial Thickness (2.5 μm)	
		After Preservation at 69°C for three months	After PCT (120°C, 2 atms, 10 hours)
80°C, 30 minutes	5.90	-0.80	-1.00
120°C, 30 minutes	4.10	-0.50	-0.80
120°C, 45 minutes	4.00	0.02	0.08
120°C, 60 minutes	3.20	0.03	0.11
120°C, 180 minutes	1.40	0.08	0.16

Table 1 (continued)

Baking Conditions	Residual Solvent Content in Film (%)	Change (μm) in Thickness from Initial Thickness (2.5 μm)	
		After Preservation at 69°C for three months	After PCT (120°C, 2 atms, 10 hours)
150°C, 180 minutes	0.80	0.08	0.16
180°C, 180 minutes	0.60	0.08	0.16

Experiment 2

[0028] A SiO_2 film having a thickness of 5 μm was formed on a 5-inch Si wafer substrate by thermal oxidation. A 2.5- μm thick polyether amide film of HIMAL HL-1200 (Trade Name by Hitachi Chemical Co.) was formed as in Experiment 1. The solvent was preliminarily removed at 70°C for 30 minutes. The preliminarily dried substrate was baked under the conditions shown in Table 2 to prepare Samples 1 to 5. The residual solvent content in these films was determined by gas chromatography. These films were immersed in ethyl cellosolve for 4 hours to observe the state of the film and to measure the change in the film thickness.

[0029] Table 4 shows that the polyether amide films (Samples 4 and 5), which were baked at a temperature higher than the glass transition temperature (230°C) so as to control the residual solvent content to 0.5% or less, have high resistance against crack formation and dissolution in the polar ethyl cellosolve solvent. Samples 4 and 5 were subjected to the preservation test at 60°C and the PCT (120°C, 2 atm, 10 hr) using the testing ink as in Example 1. The film thickness was not decreased in the testing ink.

Table 2

Sample	Baking Conditions	Residual Solvent Content (% by weight)	Change after immersing in Ethyl Cellosolve for 4 hours	Change in Film Thickness from Initial Thickness (μm)
1	120°C, 30 min	4.1	Many cracks and voids formed	-0.3
2	120°C, 45 min	4.0	Many cracks and voids formed	-0.3
3	180°C, 180 min	0.6	Many cracks and voids formed	-0.1
4	240°C, 180 min	0.5	No change	+0.2
5	300°C, 180 min	0.2	No change	+0.2

Example 1

[0030] An ink-jet head was prepared according to the following process and subjected to discharging tests.

[0031] As shown in Figs. 1 and 2, a 5-inch silicon wafer as a substrate 101 was thermally oxidized to form a 2.5- μm thick SiO_2 film as a heat-accumulating layer 102. A 0.15- μm thick exothermic element 103 composed of HfB_2 was formed on the heat-accumulating layer 102 by a sputtering process. Then, a titanium (Ti) layer with a thickness of 0.005 μm and an aluminum (Al) layer with a thickness of 0.5 μm were continuously deposited thereon to form an electrode layer 104 by an electron beam deposition process. The electrode layer 104 was patterned by a photolithographic process, as shown in Figs. 1 and 2. The resulting heating zone 201 of the exothermic element 103 had a width of 30 μm , a length of 150 μm , and a resistance, including that of the aluminum electrode, of 150 Ω .

[0032] Silicon oxide (SiO_2) was deposited on the entire substrate 101 to form a first protective layer 105 with a thickness of 2.2 μm . Thallium was deposited on the entire surface of the first protective layer 105 by a sputtering process and then patterned to form a second protective layer 106 with a thickness of 0.5 μm .

[0033] As shown by the hatching pattern in Figs. 1 and 2, a polyether amide layer 107 with a thickness of 2.5 μm was formed on the Ta second protective layer 106 by the following process.

[0034] The substrate 101 having the second protective layer 106 was cleaned and dried. A polyether amide solution having a viscosity of 500 cP was coated onto the second protective layer 106 using a spinner. After drying it at 70°C for

30 minutes, the polyether amide layer was baked under the conditions shown in Table 3 to prepare Samples A, B and C.

[0035] After the baking, a novolak positive photoresist OFPR800 (Trade name by Tokyo Ohka Kogyo Co., Ltd.) with a thickness of 12 μm was coated on the polyether amide film using a spinner, and prebaked. The photoresist layer was exposed using a mask aligner, and developed to form a predetermined pattern. The substrate was placed into an oxygen plasma ashing system to ash the polyether amide. The ashing rate of the polyether amide was 0.2 $\mu\text{m}/\text{min}$ without being affected by the baking conditions. The polyether amide with a thickness of 2.5 μm was ashed for 15 minutes in the oxygen plasma atmosphere. Next, the substrate was immersed into a remover (Sipray 1112A), and the residual photoresist layer was removed by ultrasonic energy. The polyether amide film had a thickness of 2.5 μm after removal of the photoresist layer. The ashed section of the polyether amide film, near the thermal effect section, had a shape shown in Fig. 2 and a size of 50 $\mu\text{m} \times 250 \mu\text{m}$.

[0036] The wafer was cut into individual head substrates, and a glass top board 108 having grooves with a width of 50 μm , a depth of 50 μm and a length of 2 mm was bonded onto each of the cut substrates to form ink channels 109, as shown in Fig. 3.

[0037] Pulses of 30-volts, 10- μsec , and 3-kHz were applied to the electrothermal transducers of the resulting ink-jet head. Droplets of the ink stored in the orifices were stably discharged in response to the applied signals. This operation was continued until the head did not discharge the ink droplets due to disconnection caused by electrolytic corrosion of the aluminum electrode and broken insulation between the protective layer and the aluminum electrode. The number of the repeated cycles was used as a measurement of durability.

[0038] Durability was compared using three polyether amide samples (Samples A, B and C) baked under different conditions and a Photoneece (polyimide) sample. The results are shown in Table 3.

Table 3

Sample	Baking Conditions	Residual Solvent Content (% by weight)	Print quality		
			After less than 10^7 cycles	After 10^7 to 10^9 cycles	After more than 10^9 cycles
A	120°C, 30 min	4.1	Good	Not good	Not good
B	120°C, 45 min	4.0	Good	Good	Good
C	180°C, 180 min	0.6	Good	Good	Good
Photoneece (PI)	400°C	-	Not good	Not good	Not good

[0039] Table 3 shows that the heads in accordance with the present invention, that is, Samples B and C, in which the residual solvent content in the polyether amide film is 4.0 percent by weight or less, have high durability, that is, good printing quality after more than 10^9 repeated cycles. In contrast, in Sample A and the Photoneece sample, electrolytic corrosion of the aluminum electrode due to immersion of the ink through pinholes in the SiO_2 or thallium sputtered layer is noticeable. Electrolytic corrosion of the Photoneece sample is particularly noticeable and thus deterioration of the quality of the print is significant.

Example 2

[0040] Using a polyether amide film formed under the baking conditions for Samples 3 to 5 in Experiment 2, ink-jet heads for discharging tests were produced under a process disclosed in Japanese Patent Application Laid-Open No. 61-154947 in which a solid layer was provided on an ink channel pattern of a substrate, at least a part of a channel-forming member was provided thereon, and the solid layer was removed from the substrate. A polyether amide protective layer was formed on the substrate as in Experiment 2, a photoresist PMER P-AR900 (trade name by Tokyo Ohka Kogyo Co., Ltd.) with a thickness of 30 μm was applied onto the substrate, and patterned to form ink channels. The pattern was covered with an epoxy photo-curable resin. The epoxy resin was exposed at a dose of 8.5 J/cm^2 to be cured, and the substrate was cut using a dicing machine to form discharge nozzles. The PMER P-AR900 photoresist was removed in ethyl cellosolve as a polar solvent.

[0041] The resulting ink-jet heads were subjected to the continuous discharging tests as in Example 1. The results are shown in Table 4, wherein Samples 3 to 5 in Table 4 correspond to Samples 3 to 5 in Table 2, respectively.

[0042] Table 4 demonstrates that Samples 4 and 5 having a residual solvent content in the polyether amide film of 0.5 percent by weight or less shows high print quality after more than 10^9 operation cycles. Thus, these ink-jet heads are

suitable for a multiple head. The print quality of Sample 3 is significantly inferior to that of Samples 4 and 5 after 10^7 to 10^9 printing cycles, although no problem in durability occurs. After 10^9 printing cycles, electrolytic corrosion of the aluminum electrode due to immersion of the ink through pinholes in the SiO_2 or thallium sputtered layer is noticeable.

Table 4

Sample	Baking Conditions	Residual Solvent Content (% by weight)	Print Quality		
			After less than 10^7 cycles	After 10^7 to 10^9 cycles	After more than 10^9 cycles
3	180°C, 180 min	0.6	Good	Not good	Not good
4	240°C, 180 min	0.5	Good	Good	Good
5	300°C, 180 min	0.2	Good	Good	Good

[0043] Accordingly, a highly reliable multiple head can be produced by the process disclosed in Japanese Patent Application Laid-Open No. 61-154947, by baking the polyether amide at a temperature higher than the glass transition temperature thereof and by controlling the residual solvent content to 0.5% or less.

Example 3

[0044] Two ink-jet heads were produced using ink-jet head substrates having polyether amide films formed under the baking conditions for Samples 4 and 5 in Experiment 2 by the following process, and subjected to discharging tests.

[0045] With reference to Fig. 4, a polyether amide protective layer was formed on each substrate 101 as in Experiment 2, and a polysulfone grooved top board 108 was precisely placed on the substrate 101 so that each exothermic element corresponds to an ink channel. The grooved top board 108 and the substrate 101 were fixed using a phosphor bronze presser bar spring 110. The polyamide film was patterned so as to extend to the section in contact with the top board. The print quality of these heads was high after discharge durability tests.

[0046] In the above-mentioned examples, each head has an edge shooter configuration in which ink is discharged substantially parallel to the exothermic element. The present invention is also applicable to a side shooter-type head.

Example 4

[0047] In a bubble-jet head for generating an ink discharging force using an exothermic element, forming a bubble by membrane boiling of ink to discharge the ink, an inorganic insulating layer composed of SiN or SiO_2 and a thallium anti-cavitation layer are generally provided on the exothermic element to reduce damage due to cavitation caused by electrolytic corrosion of the ink and defoaming of the bubble. Since the thallium film has low bonding force to a resin as an ink channel component, detachment of the ink channel component from the thallium film will occur.

[0048] A possible method for improving the bonding force is removal of the thallium film at the portion for providing the ink channel component. In such a case, a resin is formed on the electrothermal transducer with only the inorganic insulating layer provided therebetween. Since the inorganic insulating layer is generally porous and permeates ions contained in the resin, these ions will cause electrolytic corrosion of the electrothermal transducer.

[0049] The substrate may be subjected to treatment using a silane coupling agent or may be provided with an overlying resin layer composed of a polyimide (for example, Photoneece made by Toray Industries, Inc.) to improve the bonding force between the substrate having an ink-discharging force generating element and the ink channel component.

[0050] Separation between the substrate and the ink channel component caused by ink must be avoided during operation under ordinary conditions. Weakly alkaline inks, which have been recently used due to the required use of a variety of recording sheets and water resistance of inks, will decrease the bonding force between the substrate and the ink channel component during long-term use.

[0051] A polyether amide resin layer as the bottom layer of the substrate can maintain high bonding force for long periods even when an alkaline ink is used and even when the metal such as thallium is exposed on the bonding face, as described below.

Experiment 3

[0052] A polyether amide resin layer was provided between a substrate and a nozzle material and the bonding force was evaluated using a weakly alkaline ink by an accelerated test. Hereinafter, the polyether amide resin layer is referred to as a bonding layer.

[0053] A 5-inch silicon wafer was thermally oxidized to form a 1.0- μm SiO_2 layer. A N-methylpyrrolidone/butyl cellosolve acetate solution of a polyether amide resin HIMAL1200 made by Hitachi Chemical Co., Ltd. was coated thereon by a spin coating process, and heated at 100°C for 30 minutes and then at 250°C for one hour to form a bonding layer with a thickness of 1.5 μm . The heating of the thermoplastic polyether amide was performed to evaporate the solvents and to reduce internal stress at a temperature higher than the glass transition temperature (230°C).

[0054] A dry film resist RISTON (trade name by DuPont) with a thickness of 20 μm was laminated on the substrate and patterned using a mask aligner PLA600 to form a line-and-space pattern with an interval of 30 μm . The substrate was heated at 150°C for one hour to completely cure the pattern.

[0055] A sample not having a bonding layer and a sample having a 1.5- μm thick bonding layer composed of a polyimide Photoneece UR3100 made by Toray Industries, Inc. and baked at 400°C were also prepared for comparison.

[0056] These samples were immersed into an ink composed of ethylene glycol/urea/isopropyl alcohol/black pigment/water = 5/3/2/3/87 parts by weight and then were subjected to PCT at 120°C in 2 atm for 50 hours to observe a change in the line-and space pattern. The ink contained urea as a humectant for suppressing evaporation of the ink and preventing clogging in the nozzle, and was weakly alkaline due to hydrolysis of the urea.

[0057] In the sample having the polyether amide bonding layer in accordance with the present invention, the pattern shape did not change after the PCT test. In contrast, in the sample not having the bonding layer, an interference fringe or separation were observed in a part of the pattern, probably due to insufficient bonding between the SiO_2 layer and the nozzle material. In the sample having the polyimide bonding layer, the polyimide layer disappeared by dissolution.

[0058] Accordingly, the polyether amide bonding layer in accordance with the present invention has high bonding force and high ink resistance.

Experiment 4

[0059] The following is an example using a substrate having a SiN layer and a Ta layer and an epoxy resin nozzle material (ink channel component). A 1.0- μm thick SiN film and a 0.25- μm thick thallium film were formed on a 5-inch wafer as a substrate by a plasma enhanced CVD process. A polyether amide film was formed as in Experiment 3, and a solution of the following epoxy resin composition was applied on the polyether amide film and then patterned.

•Epoxy resin EHPE (trade name by Diacel Chemical Industries Ltd.)	100 parts by weight
•Resin 1.4-HFAB (trade name by Central Glass Co., Ltd.)	20 parts by weight
•Silane coupling agent A-187 (trade name by Union Carbide Japan KK)	5 parts by weight
•Optical cationic polymerization catalyst SP170 (trade name by Asahi Denka Kogyo K.K.)	2 parts by weight

[0060] This composition was patterned by cationic polymerization of the epoxy resin by light irradiation of a dose of 3.0 J/cm² using a mask aligner MPA600 made by Canon Kabusiki Kaisha, heated at 90°C for 30 minutes on a hot plate, developed in a methyl isobutyl ketone/xylene mixed solvent, and heated at 180°C for one hour to completely cure the resin. A line-and-space pattern with a thickness of 20 μm and an interval of 30 μm was thereby formed, as in Experiment 3. The sample was subjected to a PCT to observe a change in the line-and space pattern. No change in the pattern was observed in this sample having the polyether amide bonding layer in accordance with the present invention. In contrast, in a sample not having a bonding layer, an interference fringe and separation, probably caused by insufficient bonding force between the Thallium layer and the nozzle material, were observed in a part of the pattern.

[0061] An ink-jet head was prepared by the following procedure.

[0062] With reference to Fig. 5, a TaN electrothermal transducer 2 for generating pressure was formed on a silicon wafer substrate of a (100) crystal axis having an ink nozzle mask 3. Also, a SiN layer 4 and a thallium layer 5 were formed as protective layers. The electrothermal transducer 2 was connected to electrodes for inputting control signals (not shown in the drawing). Fig. 6 is a cross-sectional view taken along line VI-VI in Fig. 5.

[0063] With reference to Fig. 7, a polyether amide bonding layer 6 with a thickness of 2.0 μm was formed on the substrate 1 as follows. The polyether amide used was HIMAL1200 made by Hitachi Chemical Co., Ltd. The polyether amide was coated on the substrate 1 using a spinner and baked at 100°C for 30 minutes and then at 250°C for one hour.

[0064] A positive resist OFPR800 made by Tokyo Ohka Kogyo Co., Ltd. was patterned on the polyether amide, and then the polyether amide layer was patterned by oxygen plasma ashing through the resist mask. The resist mask was removed to form a bonding layer 6.

[0065] With reference to Fig. 8, an ink channel pattern 7 with a thickness of 12 μm composed of a positive resist ODUR made by Tokyo Ohka Kogyo Co., Ltd. was formed on the substrate 1.

[0066] With reference to Fig. 9, an epoxy resin layer 8 was formed on the substrate 1, as in Experiment 4, and patterned to form discharge nozzles 9.

[0067] With reference to Fig. 10, the silicon substrate 1 was subjected to anisotropic etching to form an ink supply port 10.

[0068] With reference to Fig. 11, the SiN layer 4 above the ink supply port 10 and the ink channel pattern 7 were removed, and then the substrate was heated at 180°C for one hour to complete curing of the epoxy resin 8. The epoxy resin 8 as a nozzle component was bonded to the surface (thallium + SiN) of the substrate 1 with the bonding layer 6 provided therebetween.

[0069] An ink-jet head without a bonding layer 6 was also prepared for comparison. Thus, the nozzle component 8 of the comparative ink-jet head was directly bonded to the surface (thallium + SiN) of the substrate 1.

[0070] These ink-jet heads filled with the ink described in Experiment 3 were subjected to preservation tests at 60°C for three months. The ink-jet head of this example having the bonding layer did not show an interference fringe and separation at the bonded interface of the nozzle component. In contrast, the comparative ink-jet head without a bonding layer formed a partial interference fringe between the thallium layer and the nozzle component. Accordingly, the polyether amide bonding layer in accordance with the present invention has high bonding strength in an ink-jet head which can be used in practice.

Example 5

[0071] When a polyether amide film is used as the surface layer of a substrate, the substrate can be bonded to an ink channel component by the polyether amide film provided therebetween, as described in detail below.

[0072] A 2.5- μm thick SiO_2 film as a heat-accumulating layer was formed on a 5-inch silicon wafer substrate by thermal oxidation. A 0.15- μm thick HfB_2 layer was formed on the silicon wafer substrate by a sputtering process to form an exothermic element. A 0.005- μm thick thallium layer and then a 0.5- μm thick aluminum layer were deposited thereon by an electron beam deposition process to form electrode layers. The electrode layers were patterned by a photolithographic process, as shown in Fig. 1. The heater 201 in Fig. 1 had a width of 30 μm , and a length of 150 μm . The resistance of the heater including the aluminum electrode was 150 Ω .

[0073] SiO_2 with a thickness of 2.2 μm was deposited on the entire surface of the substrate by a sputtering process to form a first protective film. Next, thallium with a thickness of 0.5 μm was deposited on the entire surface thereof by a sputtering process to form a second protective layer, and then patterned.

[0074] Next, a 3- μm thick polyether amide layer as a protective layer 107 was formed on the hatched portion in Fig. 1, as follows. The substrate 101 having the second protective layer 106 was cleaned and dried. A polyether amide (HIMAL) solution having a viscosity of 500 cP was coated onto the second protective layer 106 using a spinner. After drying it at 70°C for 30 minutes, the polyether amide layer was baked at 70°C for 3 hours.

[0075] After the baking, a novolak positive photoresist OFPR800 (Trade name by Tokyo Ohka Kogyo Co., Ltd.) with a thickness of 12 μm was coated on the polyether amide film using a spinner, and prebaked. The photoresist layer was exposed using a mask aligner, and developed to form a predetermined pattern. The substrate was placed into an oxygen plasma ashing system to ash the polyether amide. The ashing rate of the polyether amide was 0.2 $\mu\text{m}/\text{min}$ without being affected by the baking conditions. The polyether amide with a thickness of 2.5 μm above the heater 201 was removed by ashing for 15 minutes in the oxygen plasma atmosphere. Next, the substrate was immersed into a remover (Sipray 1112A), and the residual photoresist layer was removed by ultrasonic energy. The ashed section of the polyether amide film, near the thermal effect section, had a shape shown in Fig. 1 and a size of 50 $\mu\text{m} \times 250 \mu\text{m}$.

[0076] With reference to Fig. 12, a grooved top board was bonded to the upper face of the substrate. The grooved top board consisted of a glass board 500 and a polyether amide film 600 with a thickness of 50 μm formed thereon. The polyether amide film 600 was formed by two cycles of spin coating of a polyether amide (HIMAL) solution with a viscosity of 900 cP, drying at 70°C for 30 minutes, and then baking under the conditions A and B in Table 2.

[0077] A resist was applied onto the other surface not having the polyether amide film 600 of the glass substrate 500, and patterned. The glass board 500 was patterned using an aqueous mixture of hydrofluoric acid and ammonium fluoride to form an ink supply port. After removing the resist, the top board was cut using a dicer. Ink channels 230 having a width of 50 μm , a depth of 40 μm , and a length of 2 μm were formed on the polyether amide film 600 by cutting.

[0078] Since ink channels are formed by direct cutting of a glass plate in conventional technologies, cracking and chipping inevitably occur. The polyether amide layer 600 in accordance with the present invention, however, can be cut without cracking or chipping.

[0079] The substrate 430 was placed on a hot plate at 300°C, and the grooved top board 500 was placed and aligned on the substrate 430. The grooved top board 500 was pressed for 10 seconds using a heater at 300°C to weld the grooved top board 500 with the substrate 430.

[0080] In this example, the polyether amide layer was also provided at the portion of the substrate 430 corresponding to bottom walls of nozzles to facilitate bonding of the top board 500 provided with the nozzles to the substrate 430. The polyether polyamide layer absorbs a large difference in level caused by wiring on the substrate 430, and thus can facilitate bonding of the grooved top board 400 to the substrate 430, although such bonding can be achieved by welding of the polyether amide layer coated on the top board 500 even when the substrate 430 does not have the polyether amide layer.

[0081] Pulses of 30-volts, 10- sec, and 3-kHz were applied to the electrothermal transducers of the resulting ink-jet head. Droplets of the ink stored in the orifices were stably discharged in response to the applied signals. The quality of the print was satisfactory. The polyether amide layer did not cause problems, such as separation.

Example 6

[0082] With reference to Figs. 13 and 14, a substrate 410 was produced as in Example 5. A polyether amide (HIMAL) solution having a viscosity of 900 cP was applied twice on the substrate 410 by a spin coating process, dried at 70°C for 30 minutes, and then baked at 120°C for 3 hours. The resulting polyether amide film had a thickness of 30 μm. A resist pattern was formed in the polyether amide film. An ink channel was formed by an oxygen plasma process, and then the resist pattern was removed.

[0083] An etching resist PMERP-RF30S (trade name, by Tokyo Ohka Kogyo Co., Ltd.) was applied onto a copper plate, an ink channel 800 was patterned, and then the resist was removed. Discharge nozzles 250 were formed using a YAG (yttrium-aluminum-garnet) laser, and the surface of the copper plate was plated with gold. An orifice plate 700 was thereby formed.

[0084] The substrate 410 and the orifice plate 700 were aligned and bonded to each other. These were placed onto a hot plate at 300°C, and then the orifice plate 700 was pressed for 10 seconds using a heater at 300°C to weld it with the substrate 410. An ink-jet head was thereby formed as shown in Fig. 14.

[0085] Pulses of 30-volts, 10- sec, and 3-kHz were applied to the electrothermal transducers of the resulting ink-jet head. Droplets of the ink stored in the orifices were stably discharged in response to the applied signals, as in Example 5. The quality of the print was satisfactory. The polyether amide layer did not cause problems, such as separation.

Example 7

[0086] A substrate was formed as in Example 5. A polyether amide (HIMAL) solution having a viscosity of 900 cP was applied twice on the substrate by a spin coating process, and dried at 70°C for 30 minutes. The substrate was bonded to a resin orifice plate 710 shown in Fig. 15 to form ink channels and discharge nozzles. An ink channel 810 was simultaneously formed with the orifice plate 710 by molding, and then discharge nozzles 255 were formed using an excimer laser.

[0087] The substrate and the orifice plate 710 were aligned and bonded to each other. These were placed into a vacuum chamber and a load was added thereto at room temperature to evaporate a solvent, butyl cellosolve acetate, used for dissolution of the polyether amide.

[0088] Since heat was not applied for bonding of the orifice plate to the substrate, these can be tightly bonded to each other without the adverse affect of heat, such as deformation of the ink channel and discharge nozzles. Thus, the present invention is capable of using an inexpensive resin orifice plate.

[0089] Pulses of 30-volts, 10- sec, and 3-kHz were applied to the electrothermal transducers of the resulting ink-jet head. Droplets of the ink stored in the orifices were stably discharged in response to the applied signals, as in Example 5. The quality of the print was satisfactory. The polyether amide layer did not cause problems, such as separation.

[0090] While the present invention has been described with reference to what are presently considered to be the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. On the contrary, the invention is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

[0091] In an ink-jet head substrate including a thermal effect section for applying thermal energy to liquid to form a bubble in the liquid, the thermal effect section being connected with a nozzle for discharging the liquid, an electrothermal transducer for generating the thermal energy, and a pair of electrodes, a resin layer composed of a polyether amide is formed on the surface of the substrate.

Claims

1. An ink-jet head substrate comprising:

5 a thermal effect section for applying thermal energy to liquid to form a bubble in the liquid;
 a nozzle, the thermal effect section being connected with the nozzle for discharging the liquid;
 an electrothermal transducer for generating the thermal energy; and
 a pair of electrodes;
 10 wherein a resin layer comprising a polyether amide is formed on the surface of the substrate.

2. An ink-jet head substrate according to claim 1, wherein the residual solvent content in the polyether amide layer is 4% or less.

3. An ink-jet head comprising:

15 a nozzle for discharging liquid;
 a liquid channel connected with the nozzle;
 a substrate having a pressure-generating element for discharging the liquid, the liquid channel including the pressure-generating element; and
 20 a liquid channel component bonded to the substrate to form the liquid channel;
 wherein the substrate has a resin layer comprising a polyether amide resin at the bonded section to the liquid channel component.

4. An ink-jet head according to claim 3, wherein the polyether amide resin is thermoplastic.

5. An ink-jet head according to claim 3, wherein the liquid channel component comprises a resin.

6. An ink-jet head according to claim 5, wherein the liquid channel component is formed of a cationic polymerization compound of an epoxy resin.

7. An ink-jet head according to claim 3, wherein the liquid channel component is a top board having a groove for forming a part of the liquid channel.

8. An ink-jet head according to claim 7, wherein the top board is pressed and fixed to the substrate by an elastic member.

9. An ink-jet head according to claim 8, wherein the top board is formed by integral molding of a resin.

10. An ink-jet head according to claim 9, wherein the top board comprises a polysulfone or polyether sulfone.

11. An ink-jet head according to claim 3, wherein the nozzle is provided at a side away from the pressure-generating element.

12. An ink-jet head according to claim 3, wherein the pressure-generating element is an electrothermal transducer.

13. An ink-jet head according to claim 3, wherein the resin layer functions as a protective layer for the pressure-generating element.

14. An ink-jet head according to claim 3, wherein the resin layer has a residual solvent content of 4% or less.

15. An ink-jet head according to claim 3, wherein the liquid channel component and the substrate are bonded to each other by heat welding of the resin layer.

16. An ink-jet head according to claim 3, wherein the liquid channel component and the substrate are bonded to each other by vacuum drying of the resin layer.

17. A method for making an ink-jet head comprising a nozzle for discharging liquid, a liquid channel connected with the nozzle, a substrate having a pressure-generating element for discharging the liquid, the liquid channel including the

pressure-generating element, and a liquid channel component bonded to the substrate to form the liquid channel, the method comprising the steps of:

forming a polyether amide layer on the pressure-generating element of the substrate;
 forming a liquid channel pattern on the polyether amide layer using a soluble resin;
 forming a covering resin layer for forming a liquid channel wall on the liquid channel pattern;
 forming the nozzle in the covering resin layer above the pressure-generating element; and
 dissolving the liquid channel pattern.

18. A method for making an ink-jet head according to claim 17, further comprising the step of patterning the polyether amide layer by an oxygen plasma ashing process.

19. A method for making an ink-jet head according to claim 17, wherein the polyether amide resin is thermoplastic.

20. A method for making an ink-jet head according to claim 17, wherein the covering resin layer is formed of a cationic polymerization compound of an epoxy resin.

21. A method for making an ink-jet head according to claim 17, wherein the pressure-generating element is an electro-thermal transducer.

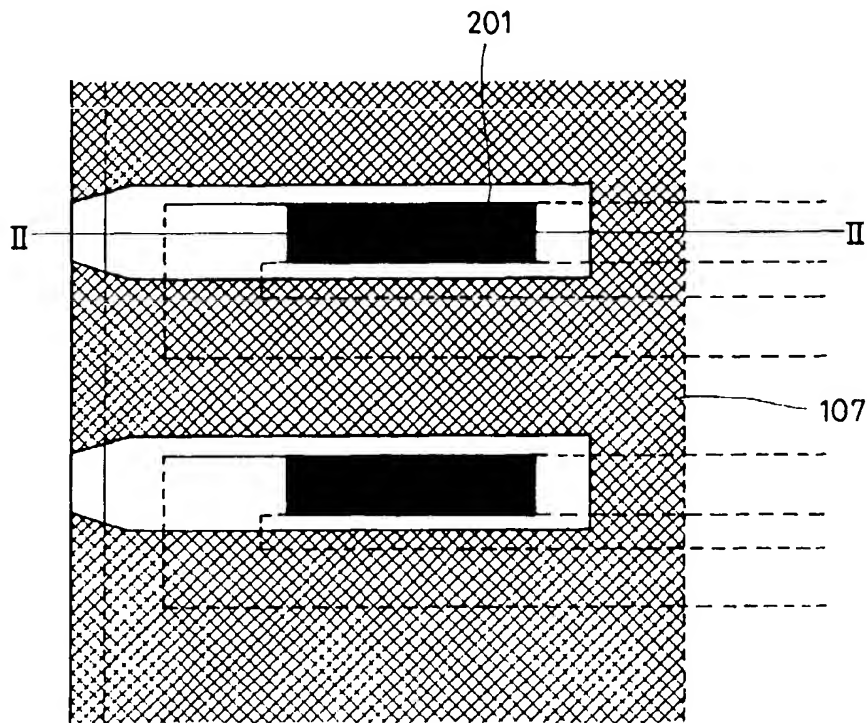


FIG. 1

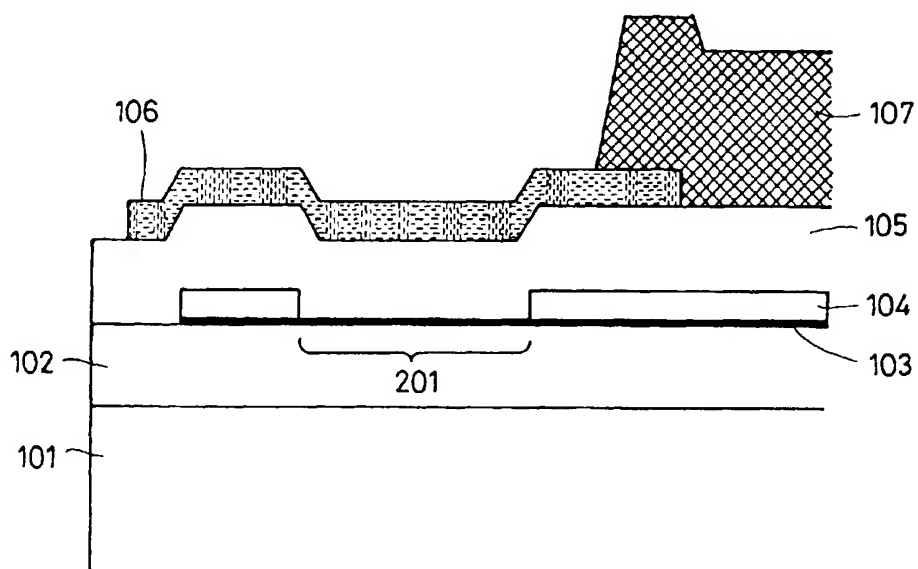


FIG. 2

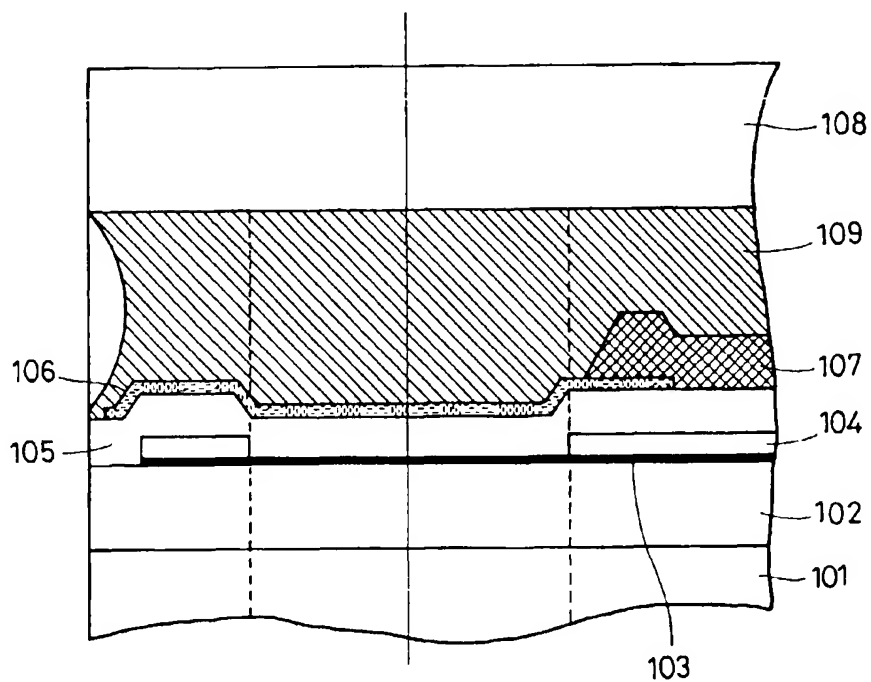


FIG. 3

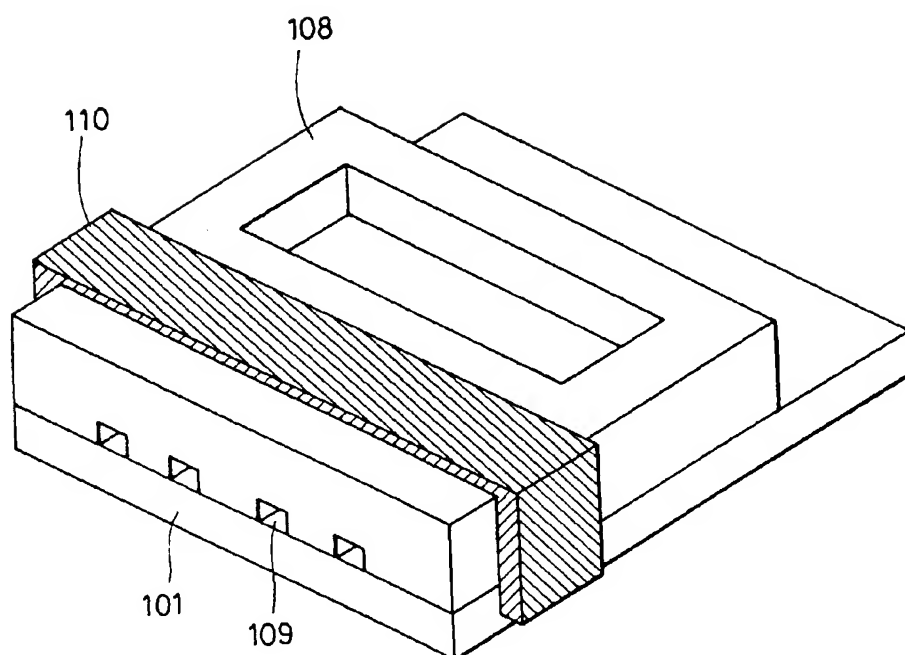


FIG. 4

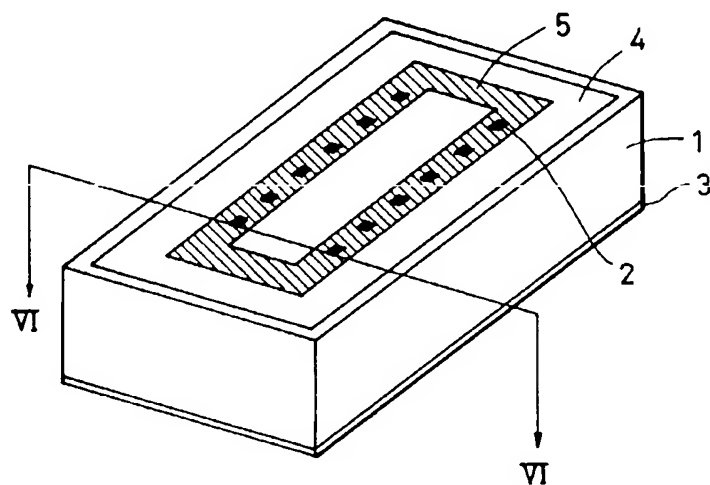


FIG. 5

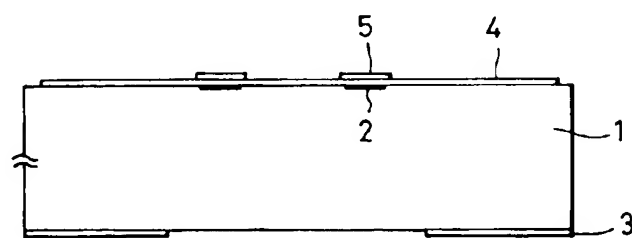


FIG. 6

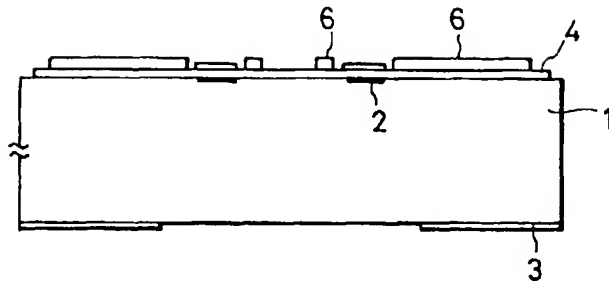


FIG. 7

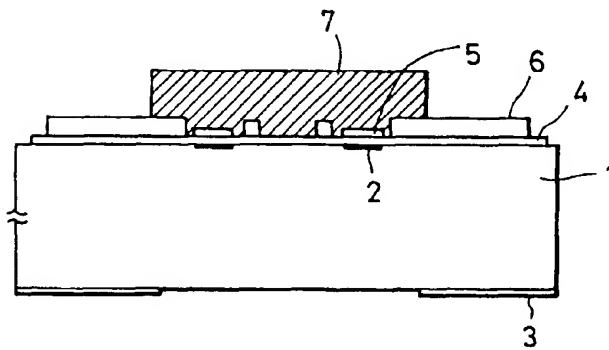


FIG. 8

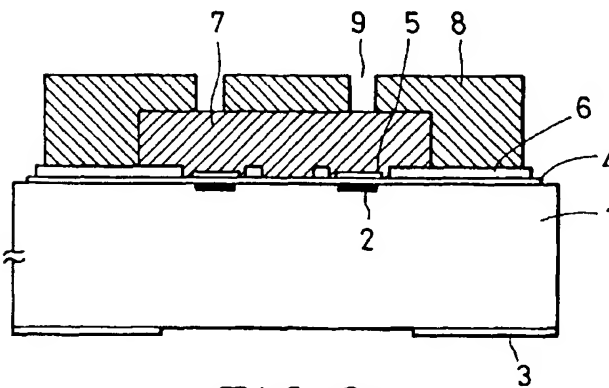


FIG. 9

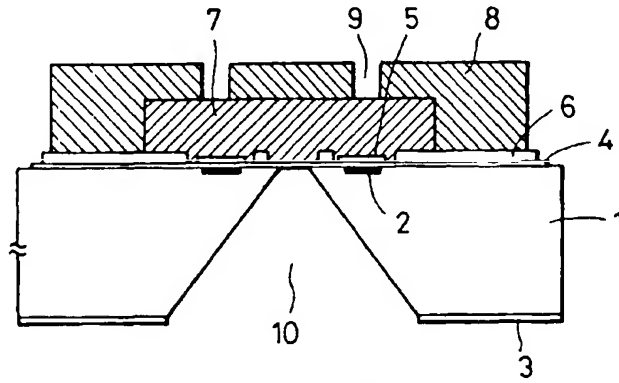


FIG. 10

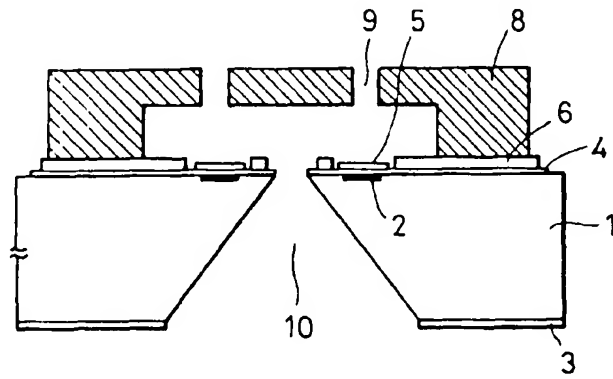


FIG. 11

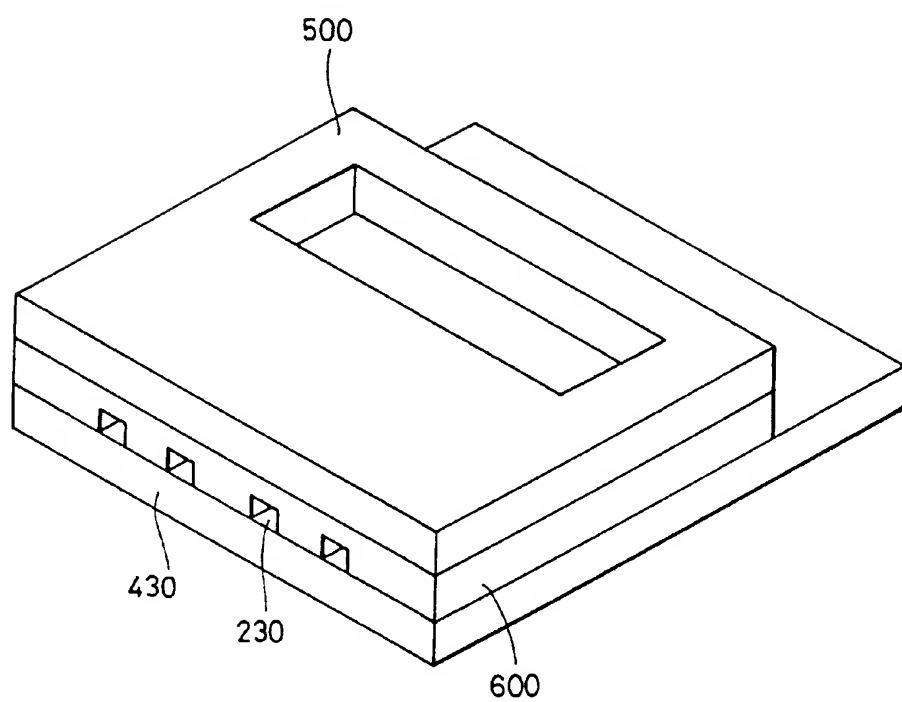


FIG. 12

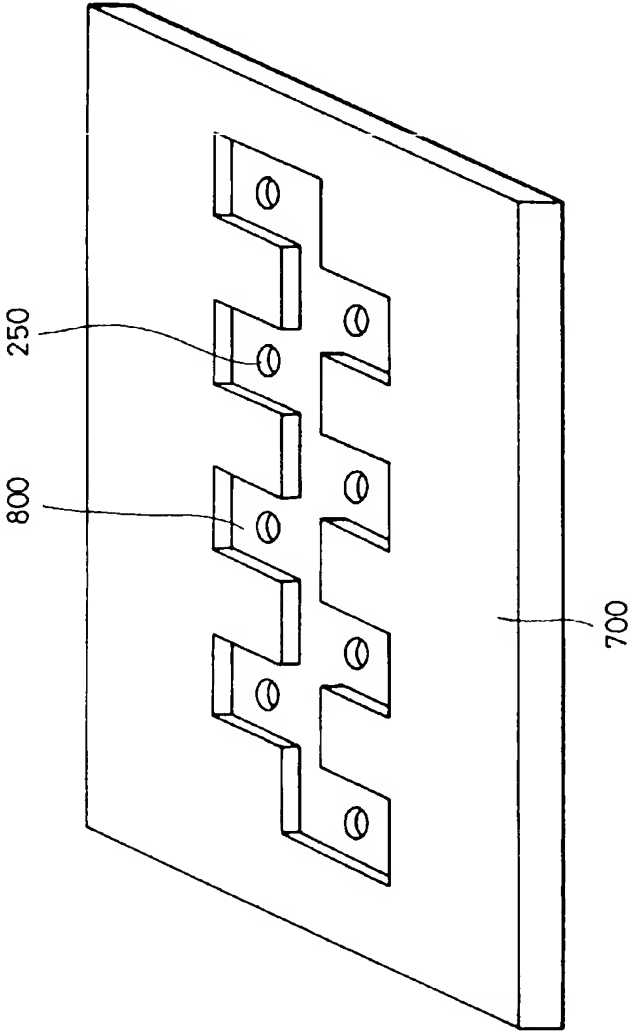


FIG. 13

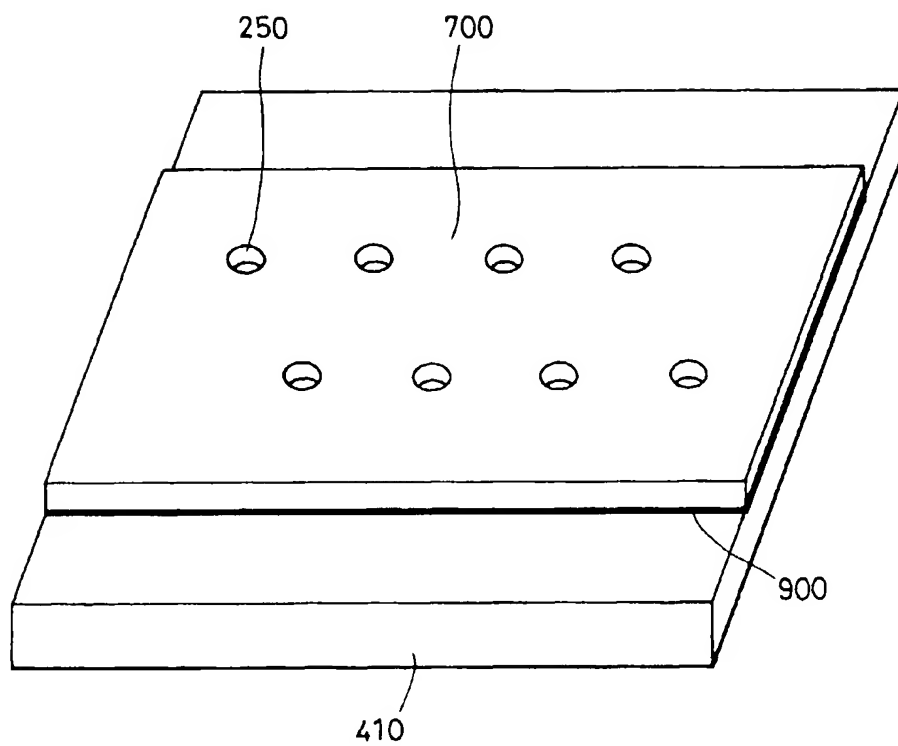


FIG. 14

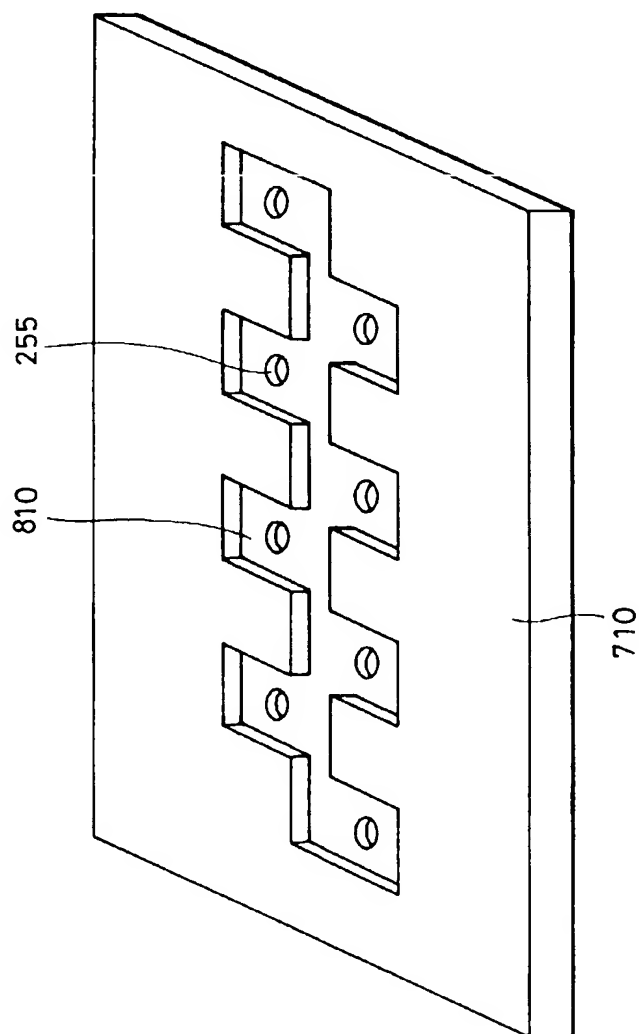


FIG. 15



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 11 0640

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 392 907 A (SHIRATO YOSHIKI ET AL) 12 July 1983 (1983-07-12) * the whole document *	1-16	B41J2/16
X	--- PATENT ABSTRACTS OF JAPAN vol. 097, no. 005, 30 May 1997 (1997-05-30) -& JP 09 001806 A (CANON INC), 7 January 1997 (1997-01-07) * abstract *	1	
X	--- EP 0 521 517 A (CANON KK) 7 January 1993 (1993-01-07) * page 8, line 14 - line 41 * * page 10, line 44 - page 11, line 40 *	1-3	
X	--- US 4 688 054 A (INAMOTO TADAYOSHI ET AL) 18 August 1987 (1987-08-18) * column 3, line 49 - column 6, line 25 * * column 10, line 16 - line 44 * * column 18, line 21 - column 20, line 28 *	1,2	
X	--- PATENT ABSTRACTS OF JAPAN vol. 097, no. 002, 28 February 1997 (1997-02-28) -& JP 08 267763 A (FUJI ELECTRIC CO LTD), 15 October 1996 (1996-10-15) * abstract *	3	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B41J
D,Y	--- US 4 657 631 A (NOGUCHI HIROMICHI) 14 April 1987 (1987-04-14) * column 3, line 46 - line 50 * --- -/--	17	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 August 1999	Examiner Van Oorschot, J
CATEGORY OF CITED DOCUMENTS		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons A: technological background O: non-written disclosure P: intermediate document &: member of the same patent family, corresponding document	
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category			

EPO FORM 1503 03.92 (P/C/C1)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 11 0640

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.8)
Y	PATENT ABSTRACTS OF JAPAN vol. 096, no. 002, 29 February 1996 (1996-02-29) - & JP 07 268095 A (IDEMITSU KOSAN CO LTD), 17 October 1995 (1995-10-17) * abstract *	17	
E	EP 0 885 723 A (CANON KK) 23 December 1998 (1998-12-23) * column 6, line 36 - line 42 *	1,3	
D,A	US 4 567 493 A (IKEDA MASAMI ET AL) 28 January 1986 (1986-01-28) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 August 1999	Examiner Van Oorschot, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background D : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 140 (01.02.1994)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 99 11 0640

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-08-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4392907 A	12-07-1983	JP 1293598 C	16-12-1985
		JP 55128466 A	04-10-1980
		JP 59031941 B	06-08-1984
		JP 1659271 C	21-04-1992
		JP 3022305 B	26-03-1991
		JP 55128468 A	04-10-1980
		JP 55128469 A	04-10-1980
		JP 1355008 C	24-12-1986
		JP 55129472 A	07-10-1980
		JP 61023832 B	07-06-1986
		DE 3011919 A	09-10-1980
		DE 3051228 C	17-12-1998

JP 09001806 A	07-01-1997	NONE	
EP 0521517 A	07-01-1993	AT 166618 T	15-06-1998
		DE 69225641 D	02-07-1998
		DE 69225641 T	26-11-1998
		ES 2118770 T	01-10-1998
		JP 5185596 A	27-07-1993
		US 5436650 A	25-07-1995
US 4688054 A	18-08-1987	JP 1766358 C	11-06-1993
		JP 4044572 B	22-07-1992
		JP 62009958 A	17-01-1987
		JP 1766360 C	11-06-1993
		JP 4044574 B	22-07-1992
		JP 62016148 A	24-01-1987
		JP 1766362 C	11-06-1993
		JP 4044576 B	22-07-1992
		JP 62016150 A	24-01-1987
		DE 3688266 A	19-05-1993
		DE 3688266 T	04-11-1993
		EP 0208300 A	14-01-1987

JP 08267763 A	15-10-1996	NONE	
US 4657631 A	14-04-1987	JP 1923936 C	25-04-1995
		JP 6045242 B	15-06-1994
		JP 61154947 A	14-07-1986
		DE 3546063 A	03-07-1986
		DE 3546794 C	31-10-1996
		US 4775445 A	04-10-1988
JP 07268095 A	17-10-1995	-----	
		NONE	

EPO FORM P0458

For more details about this annex: see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 99 11 0640

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-08-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0885723	A	23-12-1998	JP 11070658 A	16-03-1999
US 4567493	A	28-01-1986	JP 1918345 C	07-04-1995
			JP 6024855 B	06-04-1994
			JP 59194866 A	05-11-1984
			DE 3414937 A	25-10-1984
			FR 2544664 A	26-10-1984

EPO FORM P048

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

